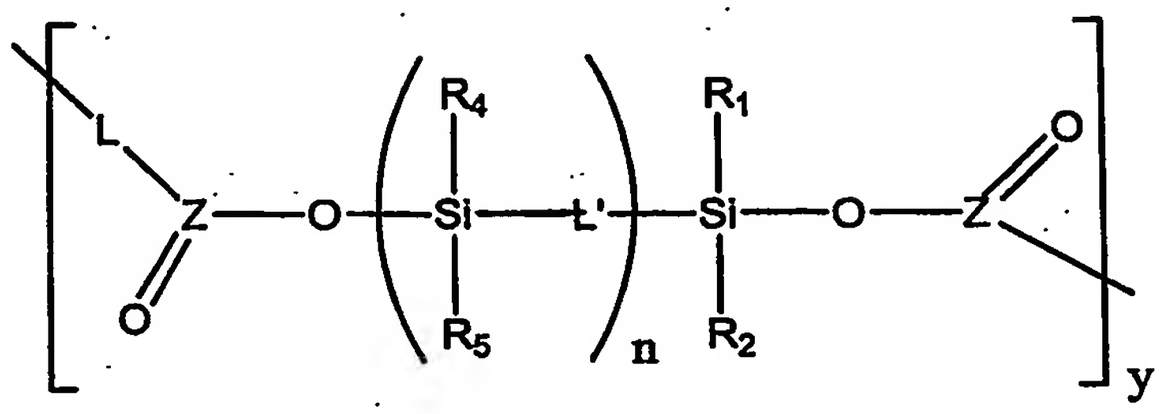
CLAIMS

1. A process for the preparation of poly(silyl ester)s comprising a structural unit of the formula (I)



(I)

wherein each R_4 and R_5 may be hydroxyl or may be independently selected from hydrogen, alkyl, cycloalkyl, aryl, alkoxyl, aryloxyl, $-L'-SiR_1R_2-$, $-L'-SiR_4R_5R_{10}$, $-L'-(SiR_4R_5L')_n-SiR_1R_2-$, alkenyl, alkynyl, aralkyl or aralkyloxyl radicals optionally substituted by one or more substituents independently selected from the group comprising alkyl, alkoxyl, aralkyl, aralkyloxyl, hydroxyl, aryl, aryloxyl, halogen, amino (preferably, tertiary amino) or amino alkyl radicals, or each R_4 and/or R_5 may independently be an $-O-Z(O)-L-$ group, where R_{10} is defined as is R_7 below,

wherein each R_1 and R_2 may independently represent hydrogen, hydroxyl, alkyl, cycloalkyl, alkenyl, alkynyl, alkoxyl, $-L'-SiR_4R_5R_{10}$, aryl, aryloxyl, aralkyl or aralkyloxyl radical optionally substituted by one or more substituents independently selected from the group comprising alkyl, alkoxyl, aralkyl, aralkyloxyl, aryl, aryloxyl, halogen, hydroxyl, amino (preferably, tertiary

amino) or amino alkyl radicals, or each R_1 and/or R_2 may independently be an -O-Z(O)-L- group,

wherein L represents a hydrocarbyl or substituted hydrocarbyl group, wherein said substituted hydrocarbyl is substituted by one or more substituents independently selected from the group comprising alkyl, cycloalkyl, carboxyl, substituted carboxyl, alkoxyl, aralkyl, aralkyloxyl, aryl, aryloxyl, hydroxyl, halogen, amino or amino alkyl radicals, or a polymer,

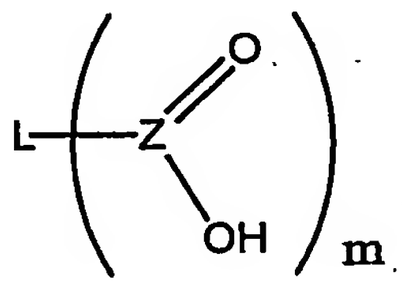
L′ represents O, S, or NR_6, $L-(NR_6-L)_p$ (where p = 1 to 10), where R_6 is defined as is R_7 below, or L,

each n independently represents a number of $-Si(R_4)(R_5)-L'-$ groups from 0 to 1000,

and y represents a number of silyl ester repeat units from 2 to 100000,

which process comprises the step of reacting;

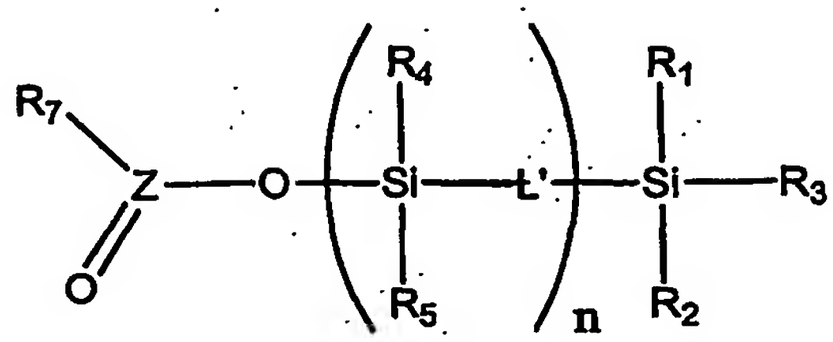
a polyacid of formula (II)



(II)

wherein Z(O)OH represents the acid moiety attached to L, m is an integer from 2 to 100000, and L is as defined above,

with a polyacyloxysilyl derivative of formula (III)



(III)

wherein R_1, R_2, R_4, R_5 , L' and n are as defined above, except R_1, R_2, R_4 and R_5 in (III) are -O-Z(O)-R_8, where R_8 is defined as is R_7 below, when the equivalent group in (I) is -O-Z(O)-L-, and R_7 is a hydrogen atom, an aralkyl, aryl, alkenyl, alkynyl, or alkyl group optionally substituted with one or more substituents selected from the equivalent substituents as defined for R_1, R_2, R_4 and R_5 above,

and R_3 is the group -O-Z(O)-R_9, where R_9 is defined as is R_7 above,

whilst removing the formed acid group(s) of formula (IV) and (V) and (VI),

R_7 Z(O)OH (IV),

R_9 Z(O)OH (V),

R_8 Z(O)OH (VI),

from the system.

2. A process according to claim 1, wherein y is 2 to 1000.

3. A process according to either of claims 1 and 2, wherein R_4 and R_5 each independently represent an alkyl, an alkoxyl, an aryl, an hydroxyl group or an $-L'-(SiR_4R_5L')_n-SiR_1R_2-$ group, wherein L', R_1, R_2, R_4 and R_5 are as defined in claim 1.

4. A process according to claim 3, wherein n = 0-100.

5. A process according to claim 3, wherein n = 0-10.

6. A process according to claim 3, wherein n is 0 or 1.

7. A process according to any preceding claim, wherein R_4 and R_5 in formula (III) are each independently selected from the group comprising an alkyl group, an hydroxyl group, an alkoxyl group or an $-L'-(SiR_4R_5L')_n-SiR_1R_2-$ group, wherein L', R_1, R_2, R_4 and R_5 are as defined in claim 1.

8. A process according to claim 7 wherein R_1, R_2, R_4 and R_5 each independently represent an alkyl group, branched or linear.

9. A process according to any preceding claim, wherein L' represents O.

10. A process according to any preceding claim, wherein Z represents C, POH, P or S=O, more preferably C.

11. A process according to claim 1, wherein R_1, R_2, R_4, R_5 and R_8 are each independently selected from the group comprising methyl, ethyl, propyl, isopropyl, isobutyl, n-butyl, sec-butyl, t-butyl, phenyl, and vinyl.

12. A process according to claim 11, wherein R_1, R_2, R_4 and R_5 are selected from the group consisting of methyl, ethyl, isopropyl, phenyl, and vinyl.

13. A process according to claim 11, wherein R_1, R_2, R_4, R_5 and R_8 are methyl.

14. A process according to any preceding claim, wherein R_6 is methyl.

15. A process according to any preceding claim, wherein the groups R_1 and R_2 are the same.

16. A process according to any preceding claim, wherein the groups R_7 and R_9 are the same.

17. A process according to claim 16, wherein R_7 and R_9 are alkyl.

18. A process according to claim 16, wherein R_7 and R_9 are methyl.

19. A process according to claim 1, wherein the polyacid of formula (II) is a polycarboxylic acid.

20. A process according to claim 19, wherein the polycarboxylic acid is a dicarboxylic acid.

21. A process according to any preceding claim, wherein L represents an alkyl, aryl, alkenyl, alkynyl, or aralkyl radical, or a polymer, preferably comprising 1 to 10000 carbon atoms.

22. A process according to claim 1, wherein L represents $-(CH_2)_n-$, and n is an integer between 1 and 10, preferably between 2 and 8, more preferably between 4 and 6, most preferably 4.

23. A process according to claim 20, wherein the dicarboxylic acid is selected from adipic acid, oxalic acid, succinic acid, glutaric acid , phthalic or isophthalic or terephthalic acids, di-lactic acid, and rosinous dicarboxylic acids.

24. A process according to claim 1, wherein the polyacyloxysilyl derivatives of formula (III) are selected from tetraisoproply-1,3-diacetoxydisiloxane, tetramethyl-1,3-diacetoxydisiloxane, dimethyldiacetoxysilane, diethyldiacetoxysilane, diphenyldiacetoxysilane, vinylmethyldiacetoxysilane, methyltriacetoxysilane, ethyltriacetoxysilane, vinyltriacetoxysilane, phenyltriacetoxysilane, tetraacetoxysilane, (butanoic acid, 1,3,5-triethyl-1,3,5-tripropyl-1,5-trisiloxanediyl ester), (1,5-trisiloxanediol, 1,3,5-triethyl-1,3,5-tripropyl-, dipropanoate), (2-silanaphthalen-2-ol, 1,2,3,4-tetrahydro-2-(7-hydroxy-1,1,3,3,5,5,7,7-octamethyltetrasiloxanoxy)-, diacetate), (2-silanaphthalen-2-ol, 1,2,3,4-tetrahydro-2-(5-hydroxy-1,1,3,3,5,5-

hexamethyltrisiloxanoxy)-, diacetate), (2-silanaphthalen-2-ol, 1,2,3,4-tetrahydro-2-(3-hydroxy-1,1,3,3-tetramethyldisiloxanoxy)-, diacetate), (1,9-pentasiloxanediol, 1,3,5,7,9-pentamethyl-1,3,5,7,9-pentavinyl-, diacetate), (1,7-tetrasiloxanediol, 1,3,5,7-tetraethenyl-1,3,5,7-tetramethyl-, diacetate), (1,7-tetrasiloxanediol, 1,1,3,3,5,5,7,7-octaethyl-, diacetate), (1,5-trisiloxanediol, 1,3,5-triethenyl-1,3,5-trimethyl-, diacetate), (heptasiloxane, 1,1,1,13-tetraacetoxy-3,3,5,5,7,7,9,9,11,11,13,13-dodecamethyl), (1,5-trisiloxanediol, 1,3,5-triethyl-1,3,5-trimethyl-, diacetate), (1,5-trisiloxanediol, 1,1,3,3,5,5,-hexaethyl-, dibutyrate), (1,5-trisiloxanediol, 1,1,3,3,5,5-hexaethyl-, dipropionate), (1,5-trisiloxanediol, 1,3,5-triethyl-1,3,5-tripropyl-, diacetate), (1,5-trisiloxanediol, 1,1,3,3,5,5-hexaethyl-, diacetate), (1,1,1,7-tetrasiloxanetetrol, 3,3,5,5,7,7-hexamethyl-, triacetate), (1,5-trisiloxanediol, 1,1,3,5,5-pentamethyl-3-vinyl-, diacetate), (1-tetrasiloxanol, 7-acetyl-1,1,3,3,5,5,7,7-octamethyl-, acetate), (1-pentasiloxanol, 9-acetyl-1,1,3,3,5,5,7,7,9,9-decamethyl-, acetate; pentasiloxanol, 9-acetyl-1,1,3,3,5,5,7,7,9,9-decamethyl-, acetate), (1,9-pentasiloxanediol, decamethyl-, diacetate), (1,5-trisiloxanediol, hexamethyl-, diacetate), (1,17-nonasiloxanediol, octadecamethyl-, diacetate), (1,15-octasiloxanediol, hexadecamethyl-, diacetate), (1,7,13-heptasiloxanetriol, tridecamethyl-, triacetate), (1,1,7-tetrasiloxanetriol, 1,3,3,5,5,7,7-heptamethyl-, triacetate), (1,13-heptasiloxanediol, tetradecamethyl-, diacetate),

(1,7-tetrasiloxanediol, 1,1,3,3,5,5,7,7-octamethyl-, diacetate), ditert-butyldiacetotoxysilane, and ditert-butoxydiacetoxysilane.

25. A process according to any preceding claim, wherein the reaction is carried out in a suitable solvent.

26. A process as claimed in claim 25, wherein the solvent is selected from pentane, cyclopentane, hexane, cyclohexane, heptane, toluene, xylene, benzene, mesitylene, ethylbenzene, octane, decane, decahydronaphthalene, diethyl ether, diisopropyl ether, diisolbutyl ether, N,N-dimethylformamide, N-methylpyrrolidone, N,N-dimethylacetamide, and mixtures thereof.

27. A process according to either of claims 25 and 26, wherein the solvent forms a heterogeneous low boiling azeotrope with the distilled acid product.

28. A process according to any preceding claim, wherein the molar ratio of the reactive groups present in the polyacyloxysilyl derivative:acid is between 1:100 and 100:1.

29. A process according to any preceding claim, wherein the solvent, where present, is at least 10 wt% of the total reaction mix at the start of the reaction.

30. A process according to any preceding claim, wherein the molecular weight is in the range 1000 to 1000000 kD.

31. A process according to claim 30, wherein the molecular weight is in the range 1000 to 100000 kD.

32. A process according to claim 30, wherein the molecular weight is in the range 1000 to 10000 kD.

33. A process according to any preceding claim, wherein m is 2.

34. A process according to any preceding claim, wherein each R_4 and R_5 may be hydroxyl or may be independently selected from alkyl, aryl, alkoxyl, aryloxyl, $-L'-SiR_1R_2-$, $-L'-(SiR_4R_5L')_n-SiR_1R_2-$, alkenyl, alkynyl, aralkyl or aralkyloxyl radicals optionally substituted by one or more substituents independently selected from the group comprising alkyl, alkoxyl, aralkyl, aralkyloxyl, hydroxyl, aryl, aryloxyl, halogen, amino (preferably, tertiary amino) or amino alkyl radicals, or R_4 or R_5 may independently be an -O-C(O)-L- group;

wherein each R_1 and R_2 may independently represent hydrogen, hydroxyl, alkyl, alkenyl, alkynyl, alkoxyl, aryl, aryloxyl, aralkyl or aralkyloxyl radical optionally substituted by one or more substituents independently selected from the group comprising alkyl, alkoxyl, aralkyl, aralkyloxyl, aryl, aryloxyl, halogen, hydroxyl, amino (preferably, tertiary amino) or amino alkyl radicals, or R_1 or R_2 may independently be an -O-C(O)-L- group,

wherein L represents a hydrocarbyl or substituted hydrocarbyl group, wherein said substituted

hydrocarbyl is substituted by one or more substituents independently selected from the group comprising alkyl, alkoxyl, aralkyl, aralkyloxyl, aryl, aryloxyl, hydroxyl, halogen, amino or amino alkyl radicals, or a polymer with pendant acid groups; and

L' represents O, S, or NR_6, where R_6 is defined as is R_7, or L.

35. A process according to any one of claims 1 to 34 which includes the additional step of incorporating the polymer in a film or coating composition.

36. A process for the preparation of poly(silyl ester)s as hereinbefore described and with reference to the examples and figure.

37. A film or coating comprising a polymer as prepared or obtainable by a process as defined in any of claims 1 to 34.

38. A poly(silyl ester) prepared or obtainable by a process as defined in any one of claims 1 to 34.

39. A coating or film composition comprising a poly(silyl ester) as prepared or obtainable by a process in accordance with any of claims 1 to 34.

40. A poly(silyl ester) comprising the repeating group (I) as defined in claims 1 to 34, and wherein L is a polylactic acid or substituted polylactic acid

residue or a rosin or substituted rosin residue of a polycarboxylic acid.

41. A coating or film composition comprising a poly(silyl ester) according to claim 40.

42. A coating or film composition according to claim 39 or 41 wherein the composition is an antifouling coating or film composition.

43. A coating or film composition according to claim 39 or 41 wherein the composition is suitable for use in medical and/or veterinary applications to provide controlled release of a bioactive substance.

44. A film or coating comprising a poly(silyl ester) according to claim 40.

45. An implantable medical and/or veterinary device having a coating comprising a coating or film composition according to claims 39, 41 or 43.